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Process for cleaning articles METHOD FOR CLEANING OBJECTS

[0001] This invention relates to a <u>processmethod</u> for cleaning <u>articlesobjects</u> and materials <u>made from of metal</u>, glass, ceramics, plastic(s), or composites thereof or of textiles.

Cleaning processes methods, in which a vapor produced by heating of an active [0002] cleaning liquid is brought into contact with articles to be eleaned the to-be-cleaned objects, are employed in the cleaning of a very wide variety of articles, such as metal articles objects, industrially_manufactured articles objects, such as printed circuit boards, articles of clothing, etc., to remove undesirable foreign substances of undesired contaminants, such as fatsgreases, lapping and polishing pastes, soldering pastes, adhesives, mixtures of inorganic (e.g., salinesalty) fouling substances and organic fouling substances (e.g., ones consisting of fattygreasy residues), etc. Until recently, chlorinated hydrocarbons were typically used for such cleaning tasks. But now, because of due to their inadequate lack of environmental compatibility, and especially because ofdue to their ozone destruction potential, their carcinogenicity, and their toxic effect, theychlorinated hydrocarbons have been banned or use of them is allowed are usable only under very strictly defined conditions. One advantage of using chlorinated hydrocarbons was that such substances do not have noa flash point at commonly-occurring temperatures. Because of Due to the above-noted disadvantages, indicated they chlorinated hydrocarbons have been replaced by other hydrocarbons or solvents, such as polypropyleneglycol ethers, alcohols, acetone, and the likeetc. The latter have a flash points in the range of normally-occurring temperatures and are consequentlythus ignition hazardous. They also present another disadvantage in that they hardly remove pigment fouling or fouling withhaving ionic salts, since these solvents are very inefficient inonly poorly dissolvinge pigments and/or salts because of due to their ionic nature of the lattercharacter.

[0003] The object of underlying the invention was to further develop a generic conventional cleaning process method so that it is performable a good cleaning effect may be achieved in an environmentally compatible manner while achieving a good cleaning effect.

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Another object of the invention wasis to prepare provide a new cleaning process wherebymethod, by which mixtures of inorganic and organic fouling maycan be eliminated simultaneously removed in an efficient manner. Another additional object of the invention was represented by preparation is to provide of a processmethod for cleaning objects and materials made of metal articles and materials which is not as harsh in the results of its operation as are state of the art processes that acts more gently than previously-known methods.

[0005] The <u>previously-identified</u> objects referred to above are attained by a processmethod having the features specified in of patent Colaim 1-of the patent. Advantageous developments embodiments of the process claimed for the invention are presented inventive method are found in patent Colaims 2 to 19.

According to the invention, Aazeotropic preparations, as claimed for the invention which are usable as active cleaning liquids, yieldfirst have the advantage above all that their liquid phase effectively, because of the aqueous component, their liquid phase efficiently dissolves pigment fouling and fouling with having ionic components, such ase.g., salts, due to the water proportion if when the azeotropic preparation used as the active cleaning liquid comes into contact with the articles to be-cleaned objects in the state of being a liquid. The molecules containing lipophilic groups of the at least one additional component containing lipophilic groups, which additional component is preferably also a liquid under ambient conditions or at low treatment temperatures, ensure that a good fat-dissolving capacity of the azeotropic preparation will possess efficient lipolytic capability.

If the azeotropic preparation used as the active cleaning liquid is heated, because of its azeotropic nature (for a definition of "azeotrope" see Römpps Chemic Lexikon [Römpp's Chemical Dictionary], 9th Edition (1989), page 323) both water and the other component(s) pass(es) into the vapor phase in a composition corresponding to that of the specific azeotrope due to its azeotropic character (for the definition of "azeotrope" see Römpps Chemic Lexikon [Römpp's Chemical Dictionary], 9th Edition (1989), page 323). When Upon contacting the vapor of the azeotropic preparation comes into contact with the articles to be cleaned to be-cleaned object, a reliable cleaning and "rinsing" from the articles to be cleaned of the all fouling substances of the to-be-cleaned object removed by the cleaning process is effected takes place.

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[8000] It is particularly advantageous that the vapor, because of its high water content, is not combustible due its high water content. Precautionary measures in this connection are superfluousunnecessary in a device used for application of carrying out the inventive methodprocess claimed for the invention. The flash point of the vapor, to the extent that such a flash point exists at all, is above the temperatures normally occurring in such a cleaning processmethod, but is at least above the boiling point of the liquid and preferablyis advantageously above about 200 °C. A flash point above 200 °C is therefore of special advantage especially preferable in that because the precautionary measures to be taken in when carrying out the cleaning processmethod are less extensive than when using active cleaning liquids with having lower flash points-are used. The azeotropic preparation, which is present in the form of a vapor at least in onea part of the process claimed for the inventioninventive method, maycan be condensed into the liquid phase either on the articles to be-cleaned to-becleaned object or by lowering of the temperature, so that costly measures tofor protecting the atmosphere surrounding the device applied for carrying out the processmethod, such as are required infor conventional processes methods, may can be dispensed with eliminated to the greatest possible extent.

Hence, an additional advantage of the process claimed for the invention inventive

method is represented by the fact that very little of the azeotropic preparation employed as the active cleaning liquid is scarcely used because of consumed due to its recondensation of the liquid to the greatest extent possible. A closed loop may can thus be created in which the

azeotropic preparation used as <u>the active cleaning fluid need not</u> be replenished <u>notat</u> all or only in negligibly small amounts. <u>AnThis is additionally aided contribution to this result is made</u> by <u>the fact that making</u> the <u>inventive</u> azeotropic preparation as <u>claimed for the invention</u> employed as <u>the active cleaning liquid may be</u> free of surfactants, <u>which are deposited that precipitate</u> on the filter surface during filtration of the active cleaning liquid <u>in-conventional-processes</u> for

precipitationremoving of the fouling substances in conventional methods and require

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[0010] Surprisingly, with the process claimed for the invention inventive method, may also be used to remove complex kindstypes of fouling substances, such as dried body fluids or other fouling substances, which occurring in everyday life as a result of precipitation deposition

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reinforcementa replenishment in conventionally-used solutions.

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of fouling substances resulting from in the form of rain or snow, etc., are also removed from articles to be cleaned the to-be-cleaned objects.

[0011] The process claimed for the invention inventive method is not limited to closed systems. It maycan, for example, also be applied carried out in the form of open jet steam vapor stream cleaning.

In-selection of When selecting the inventive azeotropic preparations elaimed for the invention used employed as the active cleaning liquid and/or of the other component(s) which the preparations—contained therein, with which have molecules having with hydrophilic groups (e.g., -OH, -NH₂, -C-O-C-, -C(=O)-C-, -C(=O)-O, etc.) and lipophilic groups (e.g., CH₂—chains or C₁—to C₁₂—alkyl—, etc.), emphasis is placed on the following criteria—in addition to good cleaning power, the following criteria stand in the foreground: The moisture water content of the azeotrope consisting—of water and (a) another further component(s) or other components—must be so high enough so—that there is no flash point, that is, so—that and/or that the vapor is not combustible. The liquid and the vapor formed from it—by heating the liquid must may neither not be toxic nor have an ozone destruction potential, nor may it they trigger a water hazard if the preparation is inadvertently released into the environment. Water-soluble components forming homogeneous azeotropes or also water-insoluble components forming heterogeneous azeotropes are suitable.

[0013] In a preferred embodiment, the process claimed for the invention inventive method for cleaning articles objects comprises the steps in which of:

-<u>forming</u> an azeotropic preparation <u>is formed of from</u> water and at least one component <u>withhaving</u> molecules <u>havingwith</u> hydrophilic and lipophilic groups in a weight ratio (component(s) with hydrophilic and lipophilic groups): <u>of water of 0.05</u> to 99.5: 99.95 to 0.05;

the articles to be cleaned are brought at least once bringing the to-be-cleaned objects first into contact with the azeotropic preparation and allowing the liquid azeotropic preparation to drain off, including inclusive of the foreign substances contaminants from the to-be-cleaned objects removed with itthereby, is drained from the articles to be cleaned;

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-<u>removing</u> residues of the azeotropic preparation on <u>and/</u>or in the articles to be cleaned are removed to be-cleaned objects by evaporation; and

-<u>condensing</u> the vapor of the azeotropic preparation <u>is condensed</u> and <u>using</u> the azeotropic preparation recovered by condensation <u>is used</u> for a <u>repeated</u> cleaning step <u>once again</u>.

[0014] The foregoing corresponds to an especiallyThus, it is accordance with a particularly preferred embodiment of the process claimed for the invention inventive method, one in which articles to be cleaned are brought to bring the to-be-cleaned objects into contact at least once into contact-with the vapor of the azeotropic preparation and, during the duration of the contact, to allow the vapor of the azeotropic preparation is allowed to condense on the articles to be cleaned objects. For example, the articles to be cleaned mayto-be-cleaned objects can be first brought into contact with the liquid azeotropic preparation only once or several times, for example, by immersion, spraying, sprinkling irrigation or the like, processes in the state of the art alreadyby comparable methods known in the prior art forof application forcefully contacting of with a liquid. The articles to be cleaned mayto-be-cleaned objects can subsequently be brought into contact one or more times into contact with the azeotropic preparation in the form of the latter's vapor thereof. The vapor of the azeotropic preparation thereby continuously condenses normally on the articles to be cleaned to-be-cleaned objects and earries with itcarries away residues of foreign substances contaminants removed from the articles to be cleaned to be cleaned objects as it drains off. As an alternative, however, the process claimed for the invention may be applied by bringing articles to be cleaned immediately inventive method can be performed by bringing the to-be-cleaned objects into contact with a vapor of the azeotropic preparation, at least once, but-preferably however several times. In this instancecase as well, the vapor condenses during the duration of the contact on the articles to be cleaned to-be-cleaned objects and thereby removes fouling substances contaminants.

In an especially preferred embodiment of the <u>processmethod</u>, <u>use is made of an</u> azeotropic preparation <u>of made from</u> water and at least one component <u>withhaving</u> molecules <u>having with</u> hydrophilic and lipophilic groups <u>is used</u>, <u>a preparation</u> in which the weight ratio (of component(s) <u>having with</u> hydrophilic and lipophilic groups): to water is in the range of 1.0 to

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35.0: 99.0 to 65.0, and even more to be preferred preferably is in the range of 4.0 to 15.0: 96.0 to 85.0.

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Corresponding to It is in accordance with another preferred embodiment of the process claimed for the invention inventive method to is use of an azeotropic preparation in the form of a mixture of made from water and at least one additional component with having molecules having with hydrophilic and lipophilic groups as the active cleaning liquid, wherein the additional component(s) and the water forming an azeotrope in the liquid phase to vapor phase transition liquid phase/vapor phase and the azeotrope being an azeotrope with having an immiscibility gap at a temperature ranging from between 0 °C to and the temperature of the phase liquid phase to vapor phase transition liquid phase/vapor phase at standard under normal pressure. Surprisingly, it has been found, in particular, that the azeotropes with having immiscibility gaps possesshave particularly advantageous cleaning properties. Particular preference is to be given to an An azeotrope with having an immiscibility gap at a temperature ranging from 20 °C to 110 °C under at standard normal pressure is particularly preferably used.

[0017] The By the term "under normalat standard pressure", is to be understood in the specification and in the claims to mean atmospheric pressure (approximately 1 or atm; about 10⁵ Pa) is understood in the description and in the patent claims.

been arrived at forexplanation of the invention at this time, it has been found that azeotropic preparations, which maycan be used as an active cleaning liquid in the process claimed for the invention inventive method, are clear at low temperatures rangingof, for example, from 20 to 25 °C. In other words, the components are fully dissolved in each other. Specific component composition relationships Defined ratios of the composition of the components are established at each temperature in the mixed phase arise for each temperature. The phases, which are separated at highan elevated temperatures, can be converted into an emulsion, which appears milky, in appearance by means of suitable process through appropriate method steps, such as preferably treatment with through exposure to ultrasound, through intensive movement during transfer by pump-transferring or agitation, etc. This emulsion exhibits has discontinuous droplets of the organic component(s) in a continuous aqueous phase. The emulsion possesses has an excellent fat-dissolving capability on the basis of capacity due to its content of organic components

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(with having molecules having with lipophilic groups); but on the basis of however, due to the continuous aqueous phase, it also dissolves water-soluble, e.g., ionic, fouling substances contaminants, such as salts. When With further increases of the temperature of anthe azeotropic preparation is raised further, the preparation passes into the vapor phase, in which vapor phase the components are present in the specific special composition typical of the particular respective azeotrope. During condensation, the azeotropic preparation again migrates through the immiscibility gap; consequently, condensinged vapor of the azeotropic preparation is present again on the articles to be cleaned, in the form of the emulsion on the to-be-cleaned objects, which emulsion haspossesses excellent dissolving properties both for lipid and foroily contaminants as well as ionic fouling substances contaminants.

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In the light of the criteria indicated above, some organic components, which form homogenous azeotropes with water, are given preference preferred for use as organic components in azeotropic preparations that are employed for application of carrying out the process claimed for this method according to the present invention. As may is readily be discerned by ascertainable for experts in this area of the arttechnical field, the invention is nevertheless not limited to the preferred, azeotrope-forming compounds forming azeotropes.

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[0020] The preferred compounds can best be described by the following general formula:

 $R^1 - [X]_n - R^3$

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wherein:

- R¹ and R³ each represent: H independently of each other; straight-chain or branched saturated or unsaturated C₁- to C₁₈--alkyl groups, in which one or more nonadjacent -CH₂-groups maycan be replaced by -O-; saturated or unsaturated cyclic C₁- to C₈--alkyl groups, in which one or more nonadjacent -CH₂- groups maycan be replaced by -O-; hydroxy; C₁- to C₈-alkyl groups; amino, wherein one or both hydrogen group(s) maycan be replaced by C₁- to C₈--alkyl groups; and

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- X represents: -O- $\frac{1}{52}$ -C(=O)-; -C(=O)-O-; -NH-; -NR¹-; -N(-OH)-; straight-chain or branched - (C₁- to C₈-) alkylene groups, in which one or more nonadjacent -CH₂- groups $\frac{1}{100}$ be replaced by -O-; and n represents integers 1, 2, 3, etc.

In other words, the organic components of the azeotropic preparations, which may be are used in the process claimed for this method according to the present invention, may can be selected from among organic compounds that belonging to the groups of alcohols, glycols, amines, ethers, glycol ethers, esters, ketones, and amino alcohols and from among as well as N-heterocycleneics or organic acids.

In an especially a particularly preferred proceduremethod, compounds of the general formula indicated above are used as (an) organic component(s) or components of the azeotropic preparation or as (an) additional organic component(s), or components in which R¹ and R³ each independently represents saturated or unsaturated C₁- to C₁₂—alkyl groups, and with even greater preferencemore preferably saturated or unsaturated C₁- to C₈—alkyl groups, in which one or more nonadjacent CH₂ group(s) maycan be replaced by -O-; may represent hydroxy, C₁- to C₈—alkoxy and unsubstituted amino groups or amino groups substituted with alkyl groups substituted amino groups; and/or X represents -O-; - C(=O)-; -C(=O)-O-; -NH-; -NR¹-; -N(-OH)=_; -OCH(R²)-CH₂- (where in R₂ represents H or methyl); and n represents 1 or 2).

[0023] Specific examples of <u>the</u> groups represented by R^1 and R^3 are hydrogen, methyl, ethyl, n-propyl, i-propyl, n-butyl, sec-butyl, i-butyl, tert-butyl, n-pentyl, n-hexyl, n-octyl, furfuryl-2, tetrahydrofurfuryl-2, hydroxy, methoxy, ethoxy, and propoxy. Specific examples of the groups represented by $\times X$ are -O-; -C(=O)-:; -C(=O)-O-; -NH-; -NR¹-; -N(-OH)-; ethyleneoxy; and propyleneoxy.

[0024] Even more preferred processes as claimed for the methods according to the present invention employ compounds of the general formula indicated above as (an) organic compound(s) or compounds—of the azeotropic preparations or as (an) additional organic component(s), which or component(s) which are selected from among those in the group:

- $(C_1$ to C_{12} -Aalkyl) C(=0)-O $(C_1$ to C_{12} -Aalkyl);
- $(C_1$ to C_{12} - $A\underline{a}$ lkyl) O $(C_1$ to C_{12} - $A\underline{a}$ lkyl);

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- $(C_1$ to C_{12} -Aalkyl) C(=O) $(C_1$ to C_{12} -Aalkyl);
- $(C_1$ to C_{12} - $A\underline{a}$ lkyl) [N (H or C_1 to C_{12} - $A\underline{a}$ lkyl) (H or C_1 to C_{12} - $A\underline{a}$ lkyl)];
- $HO-(CH_2)_{1, 2 \dots etc.} [NH_2 \text{ or } NH(C_1-\text{ to } C_{12}-\underline{Aa}lkyl) \text{ or } N(C_1-\text{ to } C_{12}-\underline{Aa}lkyl)_2];$
- H [O CH(H or CH₃) CH₂]_{1, 2 ... etc} OH; and

- (H or C_1 - to C_{12} --Aalkyl) - [O -CH(H or CH_3) - CH_2]_{1, 2 ... etc.} - [OH or $O(C_1$ - to C_{12} --Aalkyl)].

[0025] Specific Special examples of organic components compounds, which may can be used, either singlyalone or together collectively in groups of a plurality of the mentioned compounds, named in azeotropic preparations of the active cleaning liquid, are selected from the group comprising propyleneglycol ether; <u>dipropyleneglycolmonomethylether</u>; dipropyleneglycolmono-n-propylether; tripropyleneglycolmonomethylether; 3-methoxy-3methylbutanol; furfuryl alcohol: tetrahydrofurfurylalcohol; 1-aminobutonol-2; monoisopropanolamine; 2-amino-2-methylpropanol-1; 2-amino-a2-methylpropanediol-1,3; 3-(aminomethyl-)pyridine; ethanolamine; furfurylamine; methyl lactate; isopropyl lactate; aminoacetaldehydedimethylacetal; 4-aminomorpholine; 1-methylimidazole; 1,2dimethylimidazole; 1-vinylimidazole; 1,4-diazabicyclo[2.2.2]octane (DABCO): 1,5diazabicycleo[4.3.0]non-5-ene; and 1,8-diazabicyclo[5.4.0]undec-7-ene.

Addition to It is in accordance with a further, also preferred, embodiment to add at least one cleaning booster, which does not independently vaporize, to the active cleaning liquid for the inventive method process claimed for the invention of at least one cleaning booster which does not spontaneously evaporate corresponds to another especially preferred embodiment. It or they should preferably be—distilled with the azeotropic preparation. Such cleaning boosters, which do not spontaneously evaporate independently vaporize, are known to the expertskilled person from the state—of the artprior art and therefore require no further specification enumeration at this point time.

[0027] It Likewise, it is also elaimed for the preferable in accordance with the invention that it is preferable to add at least one corrosion proofing prevention additive to the active cleaning liquid. Such additive or additives It or they should preferably be distilled with the

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azeotropic preparation. Such corrosion proofing prevention additives are particularly advantageous when articles objects made of nonferrous heavy metals or light metals are toshould be cleaned. For example, excellent cleaning of aluminum articles can be accomplished cleaned with excellent results using with—an azeotropic preparation comprising 1-methylimidazole, which It acts as an inhibitor. The cleaning of Copper parts made of copper may can also be cleaned to advantage carried out in an advantageous manner with azeotropic preparations comprising 1-methylimidazole. Brightening of the surface is achieved in the process thereby. Instead place of the above-mentioned compound—indicated, use may also be made of other corrosion proofing prevention additives and corrosion prevention inhibitors can also be added, as are known to the expertskilled person from the state of the prior art.

[0028] Especially to be—preferred, as yielding excellent cleaning results, are processes methods for cleaning articles as claimed for objects according to the invention, in which an azeotropic preparation made of water and an organic component is addedused as the active cleaning liquid. By preference In this case, the organic component is in this instance preferably a compound that is selected from among those in the group: comprising dipropyleneglycolmonomethylether; dipropyleneglycolmono-n-propylether; tripropyleneglycol monomethylether; 3-methoxy-3-methylbutanol; furfuryl alcohol; tetrahydrofurfuryl alcohol; 1-aminobutanol-2; furfuryl amine; methyl lactate and isopropyl lactate.

[0029] The <u>indicated</u> compounds indicated belong to the following groups of compounds of the general formula R^1 - $[X]_n$ - R^3 :

(A) Glycol ethers:

- organic component No. 1: dipropyleneglycolmonomethylether

$$R^1 = CH_3$$
; $R^3 = OH$; $X = OCH_2$ -CH(CH₃)-; $n = 2$;

- organic component No. 2: tripropyleneglycolmonomethylether

$$R^1 = CH_3$$
; $R^3 = OH$; $X = OCH_2$ - $CH(CH_3)$ -; $n = 3$;

- organic component No. 3: 3-methoxy-3-methylbutanol

$$R^1 = CH_3$$
; $X = O-C(CH_3)_2-(CH_2)_2$; $n = 1$:

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-_organic component No. 4: dipropyleneglycol-n-propylether $R^1 = n-C_3H_7$; $R^3 = OH$; $X = OCH_2-CH(CH_3)$ -; n = 2; (B) Alcohols: - organic component No. 5: furfuryl alcohol $R^1 = Furfuryl-2; X = O; R^3 = H; n = 1;$ 5 -_organic component No. 5: tetrahydrofurfuryl alcohol R^1 = Tetrahydrofurfuryl-2; X = O; $R^3 = H$; n = 1: (C) Amines: - organic component No. 7: 1-aminobutanol-2 $R^1 = OH$; X = sec-Buty1; $R^3 = NH_2$; n = 1; 10 -_organic component No. 8: furfurylamine $R^1 = Furfuryl-2; X = -NH-; R^3 = H; n = 1;$ - organic component No. 11: 2-amino-2-methylpropanol-1 $R^1 = CH_3$; $X = CH_3 - C - CH_2OH$; $R^3 = -NH_2$; n = 1; -organic component No. 12: 2-amino-2-methylpropanediol-1,3 $R^1 = HOCH_2$; $X = CH_3 - C - CH_2OH$; $R^3 = -NH_2$; n = 1; (D) Esters: - organic component No. 9: methyl lactate $R^1 = Hydroxyethyl; X = C(=0)O-; R^3 = CH_3; n = 1;$ -_organic component No. 10: isopropyl lactate 20 $R^1 = \text{Hydroxyethyl}; X = C(=0)\text{O-}; R^3 = \text{i- } C_3H_7; n = 1;$

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[0030] In <u>such azeotropic preparations of this kind</u> to be used as an active cleaning liquid in the <u>process claimed for the invention inventive method</u>, water and an organic component are to be addedpresent in relative amounts of (100 - x) percent by weightwt%: x percent by weightwt%. In this statementHerein, x is in the ranges from of $0 < x \le 35$, is preferably in the range $3 \le x \le 25$, and by special preference particularly preferably in the range $4 \le x \le 15$.

[0031] In another preferred processmethod, the mixture ratio of water to and the other component(s) in the azeotropic preparation is <u>substantially</u> set <u>more or less</u> at the ratio, which is present in the vapor <u>as athat</u> results <u>ofby</u> heating <u>of</u> the liquid azeotropic preparation.

In another, also preferred, embodiment, the process claimed for the [0032] invention inventive method for cleaning articlesobjects includes a step in which of using an azeotropic preparation made of water and two organic components is used as the active cleaning liquid. By particular preference use is made of the active cleaning liquid of an An azeotropic preparation eonsistingmade of water, dipropylelneglycolmono-n-propylether and an additional organic component is particularly preferably used as the active cleaning liquid. The In this embodiment, further components can also be contained in the azeotropic preparation employed as the active cleaning liquid may, of course, also contain other components, such as for example at least one cleaning booster, which does not spontaneously evaporate independently vaporize and by special preference is more preferably distillsed with the azeotropic preparation, a eleaning booster such as is known from the state of the prior art and has already been referred to in the foregoingmentioned above, and/or at least one corrosion proofingprevention additive or corrosion proofing prevention inhibitor (by special preference more preferably, one that distillsed with the azeotropic preparation), such as is also known as such or is known from the state of theprior art and has already been referred to in the foregoing mentioned above.

In accordance with this preferred embodiment, by special preference it is particularly preferred to use is made as an additional organic component of a compound in from the following group as additional organic components: 1-aminobutanol-2; monoisopropanolamine; 2-amino-2-methylpropanol-1; 2-amino-2-methylpropanediol-1,3; 3-(aminomethyl-)pyridine; ethanolamine; aminoacetaldehydedimethylacetal; 4-aminomorpholine; 1-methylimiazole; 1,2-dimethylimidazole; 1-vinylimidazole; 1,4- diazabicyclo[2.2.2]octane (DABCO); 1,5-diazabicyclo[4.3.0]none-5-ene; and 1,8-diazabicyclo[5.4.0]undec-7-ene.

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[0034] The <u>mentioned</u> organic compounds indicated maycan be used singlyalone or in combination with each other.

[0035] Also to be given particular preference is It is also particularly preferred to use of an additional organic component of the group: made up of acetic acid, hydroxyacetic acid, formic acid, and butyric acid. The indicated acids in question may can also be used individually alone or in combination with each other or with other substances, such as the organic components named above.

In accordance with the <u>above-described</u> preferred embodiment, just described use is made as active cleaning liquid of an azeotropic preparation consisting made of water, a glycol ether (preferably dipropyleneglycolmono-n-propylether) and an additional organic component is used as the active cleaning liquid in relative amounts of 90 percent by weight wt%: (10 - y) percent by weight wt%: y percent by weight wt%, where y is in the range of y is y and by special preference particularly preferably y is y and y is y and y and y and y is y and y and y are y are y and y are y are y and y are y and y are y are y and y are y are y and y are y and y are y are y and y are y are y and y are y are y are y are y and y are y are y and y are y and y are y are y and y are y are y are y are y and y are y are y are y and y are y and y are y and y are y are y and y are y are y are y and y are y and y are y are y are y and y are y and y are y and y are y

A schematic drawing is presented A device, in which the inventive method can be carried out, is schematically illustrated in the attached drawing of a device in which the process claimed for the invention may be applied appended Figure: As storago reservoir tank 2 with having a separation compartment precipitation chamber 4 and an overflow compartment chamber 6 is connected by way of via a feed pump 8 and a heating device 10 to a cleaning device 12. The interior of the cleaning device, whose structure is of the state of known in the prior art and which may can include cleaning nozzles, a revolving circulating basket, etc., is connected, in the example shown in the figure, is connected to a pressure compensation vessel 14, which is, however, is not essential for operation.

[0038] PipingA conduit leads from the bottom of the cleaning device 12 to a filter device 16. The filter device 16 is connected by way of pipingvia a conduit to with a feed pump 18 on the top_side of the separation compartment precipitation chamber 4. Additional pipingAnother conduit extends leads from the filter device 16 back to the precipitation chamber 4 via by way of a vacuum pump 20 through a condenser 22 and a cooler 24 back to the separation compartment 4.

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[0039] Piping also extends A conduit further leads from the overflow compartment 6 into a distillation device 30 by way of via a delivery feed pump 26 through a heat exchanger 28 into a distillation device 30 and thence from there back into the cleaning device 12 or back to the storage reservoir tank 2.

A feed line 32 charging the storage tank 2 with active cleaning liquid extends leads into the storage reservoir tank 2 for filling the reservoir tank 2 with the active cleaning liquid. The storage reservoir tank 2 also contains a not-illustrated device, not shown, for removal drawing off sludge that depositsed in the separation compartment precipitation chamber 4.

[0041] Ventilation piping 34 extends leads into the normally-sealed cleaning device 12.

[0042] The structure of the individual structural elements of the <u>described</u> cleaning device 12 and an electronic control <u>unit</u>-(not shown) <u>forof</u> the individual <u>structural components is of the state of the artassemblies are known</u> and <u>is consequently are therefore</u> not described in detail.

The <u>function of the described</u> device <u>described operatesis</u> as follows: After <u>charging</u> the cleaning device 12 <u>has been charged</u> with an <u>to-be-cleaned item-article or articles to be cleaned</u>, a <u>liquid cleaning takes place</u> in an exemplary but not restrictive embodiment, <u>first liquid cleaning is carried out-in</u> which the feed pump 8 is actuated and <u>the active cleaning liquid</u>, whose the temperature <u>mayof which can if desired</u> be adjusted in the heating device 10 if <u>necessary</u>, is fed <u>into</u> the cleaning device 12. In the cleaning device 12 the revolving An immersion bath of the circulating cleaning item article or articles to be cleaned is/are immersed and/or a spraying of the cleaning item article or articles to be cleaned are sprayed—with liquid takes place in the cleaning device 12. The liquid is removed from the cleaning device 12 through the filter device 16 by the feed pump 18 and is fed into the separation compartment precipitation chamber 4. Predominantly inorganic fouling substances are precipitated in the filter device 16 and are removed drawn off. Predominantly fatty fat-containing fouling substances are precipitated in the separation compartment precipitation chamber 4 and are also removed drawn off.

[0044] The <u>exemplary-described</u> liquid cleaning stage described as an example is followed by rinsing under the same conditions with active cleaning liquid from the tank 6.

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The rinsing is followed by Then, a steamvapor cleaning stage and/or steama vapor rinsing stage takes place, in which the feed pump 26 is actuated and thenso that the active cleaning liquid is heated in the distillation device 30 and is converted into vapor. Because of As a consequence of the azeotropic nature character of the azeotropic preparation employed as the active cleaning liquid, this vapor has a predetermined content of water and the additional component(s)—or components. The composition—of—the—liquid azeotropic preparation is preferably already composed from its components so that such that it they also corresponds in point of the content to the corresponding components in the vapor phase. In the cleaning device 12 the vapor comes into vigorous intensive contact with the to-be-cleaned item-article or articles to be cleaned; wherein at least a part of the vapor is condenses. The condensate is supplied by feed pump 18 delivers the condensate to the precipitation compartment chamber after this condensate has passed flowing through the filter device 16.

[0046] The liquid may be reconditioned if When the vapor is fed back into the storage reservoir tank 6 from the distillation device 30 by way of via the condenser 22 and the cooler 1424, the liquid can be purified thereby.

The vapor cleaning or vapor rinsing is advantageously followed by <u>recirculating</u> air drying or vacuum drying. In the process the The vapor present in side the cleaning device 12 is drawnthereby suctioned off by the vacuum pump 20, wherein the condensate formed in the cleaning device 12 passing flows through the filter device 16. The vapor mixed with the condensate is returned again supplied to the storage reservoir tank 2 as a liquid after passing flowing through the condenser 22 and cooler 24.

[0048] After vacuum drying has been completed, the separation compartment precipitation chamber 4 is nerated by way of ventilated via the neration ventilation line 34, and the cleaned article(s) mayitem can be removed.

In an alternative embodiment, which also yields favorable results, articles to be treated to-be-treated objects are sprayed in the cleaning device 12 with the azeotropic preparation used as the active cleaning liquid. In this process This happens in the way that articles to be cleaned the to-be-cleaned objects are soaked insaturated with the liquid. The subsequent

processmethod steps are more or lessessentially the same as thosewere described in the foregoing above.

[0050] After the treatment, the to-be-treated objects articles treated are in a distinctly better condition than after treatment in a conventional processmethod, that is, i.e. by use of using conventional organic customary solvents for the cleaning steps under identical conditions. In particular, it has been found, surprisingly, determined that not only are all organic fouling substances, in particular inclusive of lipophilic and/or oily or fatty substances, removed, but also all the inorganic fouling substances, in particular inorganic salts from perspiration, coloring pigments, etc., are removed in addition to all organic fouling substances such as lipophilic or oleaginous or fatty substances. The treated objects articles treated have no unpleasant odor and are exhibit an excellent outstanding in appearance.

[0051] As was stated earlieralready explained above, azeotropic preparations withhaving an immiscibility gap exhibit a surprisingly efficient good cleaning behavior distinctly superior to that of conventional preparations.

an immiscibility gap, in treatment in the liquid phase articles to be cleaned the to-be-cleaned objects are brought into contact with an azeotropic preparation when treating in the liquid phase, which azeotropic preparation is in a state, such that in which the components of the azeotropic preparation are present in separate, or at least partly separate, phases. For example, the liquid azeotropic preparations present in athe state of phase separation are treated with ultrasound or are vigorously intensively pump-transferred by pumping or agitated, so that a milky emulsion of the azeotropic preparation is-formsed. This emulsion efficiently effectively dissolves not only fatty or oily components, but also ionic and/or saline salty contaminants fouling substances as well.

Whenever articles to be cleaned are treated In the case of treating to-be-cleaned objects with the azeotropic preparation in the vapor phase, as described above the azeotropic preparation is heated as previously described and a vapor is produced, in which the components are present in the quantitative proportions that are determined by the characteristic azeotropic properties. The vapor condenses at least to some extentpartially on the articles to be cleaned to be-cleaned objects, and the same milky emulsion is obtained arises as in the liquid phase.

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Efficient dissolving of fats and salts An excellent oil- and salt-dissolving capacity is also observed in this instance as wellcase.

[0054] When By increasing the temperature of the azeotropic preparation is raised to the point phase transition of liquid phase/vapor phase transition, the components pass into the vapor phase in the quantitative proportion corresponding to that of the azeotrope, and the azeotropic preparation can be produced purified by distillation without any problem.

The last-named_mentioned embodiment of the process claimed for the invention inventive method is particularly favorable advantageous for the cleaning-of metal parts. Thus, for example, lapping and polishing pastes can be very efficiently highly effectively removed from metal parts by use-of using azeotropes with having an immiscibility gap. For instance, an azeotropic preparation compounded mixed with acidic additives is used as the active cleaning liquid for this purpose. The Ccleaning is carried outtakes place in the above-described one-compartment chamber system described above—and may be conducted an take place continuously or in a batch process.

Likewise, SMD adhesives (SMD = surface mounted devices), such as are employed in the manufacture of SMD components for double-sided mounting, can also be removed surprisingly well from electronic components, whereby produced in double sided assembly to prevent the components from being do not detached during the soldering process. The adhesive is eustomarily usually applied by way of via dispenser systems or templates before the printed circuit boards are secured attached. Defectively—printed or dispensed circuit boards and/or templates may can be cleaned. Surprisingly, cleaning results can be achieved with the azeotropic preparations employed according to the invention that distinctly superior to surpass those obtained with the azeotropic preparations used as claimed for the invention. In addition, precautionary measures (such as those taken to prevent explosions when correspondingly hazardous solvents are used) are superfluous unnecessary.

[0057] The azeotropic preparations indicated may be used similarly by the process claimed for the invention to remove excess In the same way, surplus soldering paste applied during soldering can be removed simply and in an environmentally friendly manner—from

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defectively_printed eircuit boards and templates in a simple and environmentally-friendly manner. It is also possible to remove excess The removal of fluxing agent residues after soldering is likewise possible. Cleaning is accomplished The cleaning takes place by spraying, spray rinsing, and drying of articles to be eleaned the to-be-cleaned objects, preferably in anthe immersion process involving with ultrasound (cleaning stage), rinsing with or without ultrasound (rinsing stage), and drying. The Ccleaning is carried out preferably at a temperature in the range of 40-60 °C, but it is not restricted to this temperature range. The temperature may be significantly higher, for example, it may even exceed 100 °C, especially in treatment of articles to be cleaned in particular when treating the to-be-cleaned objects during the cleaning stage with the vapor of the azeotropic preparation.

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[0058]

[0059]

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Particularly preference is given to use of preferably, the azeotropic preparations presented in according to the following Table I beloware used for cleaning processes as claimed formethods according to the invention. Also given in this table are the The preferred proportions of organic components (O.K.C.): to-water, the boiling points of a particular the respective azeotropic preparations, and as well as the temperatures, at which exemplary treatment of articles to be cleaned may be carried outto-be-cleaned objects can be treated in an exemplary manner, are provided in this Table. The invention is not, of course, restricted to the proportions of the <u>indicated</u> components and treatment temperatures indicated.

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particularly preferably used. An exemplary, but not restrictive limiting, composition of the azeotropes is as follows: water (90 percent by weightwt%), dipropyleneglycolmono-npropylether (10_ y percent by weightwt%), y percent by weightwt% of the compounds indicated in Table II.

dipropyleneglycolmono-n-propylether, and amine compounds and/or nN-heterocyclic compounds or organic acids, as shown in according to the following Table II beloware

particular preference is given to three-component_mixtures

[0060]

Table I

Azeotropic Preparation		Boiling Point	Treatment
		(°C)	
		(C)	Temperature
Organic Components	O.K. to Ratio		(°C)
(O. <u>C</u> K.)	O.C.: Water Ratio		
No. 1	8.9 : 91.1	99.2	60
No. 2	7.9 : 92.1	99.1	60
No. 3	11:89	99 – 101	65
No. 4	10:90	100	65
No. 5	20:80	98.5	65
No. 6	10.5 : 89.5	102	65
No. 7	4.7 : 95.3	102	65
No. 8	30.9 : 69.1	100	60
No. 9	20:80	99.5	60
No. 10	34 : 76	98	60
No. 11	5:95	98	65
No. 12	6,5: 93,5	101	60

[0061]

Table II

Organic Components	y (<u>wt</u> %- by weight)	Boiling Point (°C)
1-Aminobutanol-2	05.3	101
Monoisopropanolamine	05.8	100
2-Amino-2-methyl- propanol-1	1,23	102
2-Amino-2-methyl- propandiol-1,3	1 ₇ 5	101
3-(Aminomethyl-) pyridine	0 <u>7.</u> 16	101
Ethanolamine	0 <u>5.</u> 3	104
Aminoacetaldehyd <u>e</u> - dimethylacetal	2 _{5.} 4 3 _{5.} 4 4 _{5.} 2 0 _{5.} 4	101
4-Aminomorpholine	0,4	101
1-Methylimidazole	0,1	101
1,2-Dimethylimidazole	0,,1	100 – 102
1-Vinylimidazole	0,3	101
DABCO	0 _{7.} 03 0 _{7.} 08 0 _{5.} 1	101 – 103
1,5-Diazabicyclo- [4.3.0]non-5-en <u>e</u>	05.02	101 – 103
1,8-Diazabicyclo- [5.4.0]undec-7-en <u>e</u>	0 <u>5.</u> 02	101 – 103
Acetic Acid (80-% ig)	15.5	100 – 101
Hydroxyacetic acid	05.5	100 – 101
Formic Acid	15.5	100 – 101
Butyric Acid	15.2	100 - 101

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[0062] The boiling point (°C) of the azeotropic preparation $\frac{\text{made up of } \underline{\text{from}}}{\text{made possible}}$ water, dipropyleneglycolmono-n-propylether, and the $\underline{\text{indicated }}$ compounds $\underline{\text{indicated }}$ is also given in Table II.

[0063] The invention is illustrated will be explained by the following examples, but is not restricted to these examples without however being limited thereto.

Example 1

The drum of the cleaning device 12 described above was charged with to-be-cleaned material-to be cleaned. The material, consisting of textiles, was treated in athe first step treated under liquid cleaning conditions with azeotropic preparations at elevated temperatures. The azeotropic preparations and the pertinent respective treatment temperatures are indicated in Table I above. The material was dipped immersed into the hotwarm azeotropic preparation during agitation while being moved. The hotwarm azeotropic preparation was fed in a closed loop from the drum of the cleaning device 12 through a filter device 16 and delivered to the separation compartment precipitation chamber 4. In the filter device 16, predominantly inorganic fouling (salts) was deposited and also removed precipitated, which was drawn off. In the precipitation chamber 14, predominantly fat-containing fouling precipitated, which was likewise drawn off.

The first treatment step was followed by a second treatment step, which was also carried out under liquid treatment conditions. Fresh azeotropic preparation (see Table I for the composition; in each operation the azeotropic preparation of the second treatment step was of the same composition as that of the first step) was fedsupplied to the drum of the cleaning device 12 at an elevated temperature. The material was delivered supplied in a second closed loop from the drum of the cleaning device 12 to the separation compartment precipitation chamber 4 by way of via a filter device 16. The separation of inorganic and organic substances were separated took place in the same way as in the first treatment step.

The second treatment step was followed by a third treatment step, in which the tobe-treated material to be treated was treated with the vapor of the particular respective azeotropic preparation, the This had the composition (see Table I) of which was that typical of the

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particular respective azeotropic preparation (see Table I). After passing through the feedsupply pump, the azeotropic preparation was converted into the vapor phase in a distillation device. The vapor was brought into intimate contact with the to-be-treated material to be-treated in the drum of the cleaning device 12. Part of the vapor was condensed at the time of contact with the material. The liquid from the cleaning step following occurring after the condensation was removed from the drum and, after passing through the filter device 16-for-separation of the organic substances, was delivered supplied to the separation compartment precipitation chamber 4 for separation of the organic substances, where organic contaminants were separated. The vapor, which was not already condensed in the drum of the cleaning device 12, was withdrawn off from the drum, condensed, and (after optional filtration) delivered supplied to the storage reservoir tank 2 for futurefurther usage.

[0067] After drawing off the vapor of the azeotropic preparation had been removed, the drum was evacuated, for example atto 10-2 bar, and the remaining vapor was removeddrawn off in the same way as described above. The hot-warm-treated material released the water and the organic components of the azeotropic preparation in the vacuum, with the result that the materialso that it was dry after 10 minutes of vacuum treatment.

[0068] The to-be-treated material to be treated was in much better condition thant such material that has been treated byin the conventional meansway. Both inorganic and organic fouling substances were entirely removed in their entirety. The material gave offhad no unpleasant odor and was outstanding in an excellent appearance. It was successfully could be ironed and/or pressed with good results.

[0069] The third step (vapor treatment) is not absolutely necessarily required after liquid cleaning; equally good results just as good as those described above eanwere also be obtained with-noachieved without the vapor treatment. It is claimed for the invention that it is also possible according to the invention to completely or partially replace the steps of treatment of tobe-cleaned material to be treated, in whole or in part, bywith liquid azeotropic preparation with steps of treatment with azeotropic preparation in vapor form. Equally good cleaning results were obtained achieved with this procedure as well.

Example 2

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Defectively-printed circuit boards or templates produced in from the SMD-manufactureing were treated with a three-component mixture made of water, dipropyleneglycolmono-n-propylether and/or an amine compound and/or an N-heterocyclic compound and/or organic acids, such as is shown by way of example in Table II. The three-component mixtures, which were used as the active cleaning liquids, consisted were composed of 90 percent by weightwt% water, (10 - y) percent by weightwt% dipropyleneglycolmono-n-propylether, and y percent by weightwt% of one of the compounds listed in Table II. The Ccleaning was accomplished bytook place in the spray process.

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In order to remove SMD adhesives, the The circuit boards or and templates, respectively, were treated with the liquid azeotropic preparations for removing SMD adhesive at the boiling points temperatures indicated in Table II with liquid azeotropic preparations, the treatment being accompanied by application usage of ultrasound (ultrasound is not, however, absolutely necessarily required for obtaining achieving good cleaning results). The azeotropic preparations were in the form of a milky emulsion, which became almost clear whenduring application of ultrasound was applied. All traces A complete removal of the adhesives were removed took place, without the need for providing protective devices in the system, such as ones for protecting against explosions.

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The cleaning results were considerably better than those obtained by application of when using conventional solvents such as butyl acetate or isopropanol. In addition, in the case of the latter two, it is absolutely necessary to provide protection of the system from against explosions must necessarily be provided for labor safety reasons of workplace safety.

Claims

- 1. A processmethod for cleaning articles objects, in which a vapor produced by heating an active cleaning liquid is brought into contact with articles to be cleaned to be-cleaned objects, characterized in that there is used as active cleaning liquid an azeotropic preparation in the form of a mixture made of water and at least one additional component with having molecules havingwith hydrophilic and lipophilic groups is used, wherein the additional component(s) and the water forming an azeotrope during the phase transition liquid phase tensition.
- 2. A process as described in method according to Claim 1 comprising the steps in which:
- -_an azeotropic preparation is prepared_formed_with_from water and at least one component withhaving molecules havingwith hydrophilic and lipophilic groups; in a weight ratio (component(s) havingwith hydrophilic and lipophilic groups): to-water of 0.05-99.95 to 99.5–0.05;
- -<u>articles to be cleaned the to-be-cleaned objects</u> are brought at least once into contact with the azeotropic preparation and liquid azeotropic preparation<u>is allowed to drain off</u>, including inclusive of impurities from to-be-cleaned objects removed thereby the latter, is drained from the articles to be cleaned;
- -_residues of the azeotropic preparation on <u>and/</u>or in the <u>articles to be cleaned to-be-</u> <u>cleaned objects</u> are removed by evaporation; and
- -_the vapor of the azeotropic preparation is condensed and the azeotropic preparation recovered by condensation is used for a repeated-cleaning step_once again.
- 3. A process as described inmethod according to Claim 1 or Claim 2, wherein articles to be cleaned the to-be-cleaned objects are brought at least once into contact with a vapor of the azeotropic preparation and, during the duration of the contact, the vapor of the azeotropic preparation is allowed to condense on the articles to be cleaned to-be-cleaned objects.
- 4. A process as described inmethod according to one of Claims 1 to 3, wherein use is made as active cleaning liquid of an azeotropic preparation is used as the active cleaning

<u>liquid</u> in the form of a mixture <u>made</u> of water and at least one additional component <u>withhaving</u> molecules <u>havingwith</u> hydrophilic and lipophilic groups, <u>wherein</u> the additional component(s) and the water forming an azeotrope <u>duringat</u> the phase transition <u>from</u> liquid phase <u>late</u> vapor phase and the azeotrope <u>beingis</u> an azeotrope <u>withhaving</u> an immiscibility gap at a temperature between 0 °C and the temperature of the phase transition <u>from</u> liquid phase <u>late</u> vapor phase <u>under normalat standard</u> pressure, preferably an azeotrope <u>withhaving</u> an immiscibility gap at a temperature in the range from 20 °C and 110 °C <u>under normalat standard</u> pressure.

5. A process as described inmethod according to one of claims 1 to 4, wherein use is made, in addition to water, as additional component of the active cleaning liquid, an organic component of the general formula

$$R^{1} - [X]_{n} - R^{3}$$

is used, in addition to water, as a further component of the cleaning-active liquid, wherein: which

- R^1 and R^3 each independently represents H; straight-chain or branched, saturated or unsaturated, C_1 - to C_{12} —alkyl groups, in which one or more nonadjacent -CH₂- groups $\frac{maycan}{maycan}$ be replaced by -O-; saturated or unsaturated cyclic C_1 - to C_8 —alkyl groups, in which one or more nonadjacent -CH₂- groups $\frac{maycan}{maycan}$ be replaced by -O-; hydroxy; C_1 - to C_8 -alkoxy; amino, $\frac{in-which}{wherein}$ one or both hydrogen(s) $\frac{maycan}{maycan}$ be replaced by C_1 - to C_8 -alkyl groups; and

X represents -O-; -C(=O); -C(=O)-O-; -NH-, -NR 1 -; -N(-OH)-; straight-chain or branched)_—(-C₁- to C₈-) alkylene groups in which one or more nonadjacent –CH₂- groups maycan be replaced by -O-; and n represents integers 1, 2, 3, etc.

6. A process as described inmethod according to one of Claims 1 to 5, wherein the mixture ratio of water and the additional component(s) established in the azeotropic preparation is more or less substantially set at the ratio, which is present in the vapor that result sing from by heating of the liquid azeotropic preparation.

- 7. A process as described in method according to one of Claims 1 to 6, wherein there is added to the active cleaning liquid—at least one cleaning booster, which does not spontaneously evaporate independently vaporize, and/or at least one corrosion proofing preventing additive is added, preferably at least one cleaning booster, which does not spontaneously evaporate independently vaporize, and/or at least one corrosion proofing preventing additive which that is distill(s)ed with the azeotropic preparation.
- 8. A process as described in method according to one of Claims 1 to 7, wherein an azeotropic preparation made of water and anone organic component is used as the active cleaning liquid.
- 9. A process as described in method according to one of Claims 1 to 8, wherein there is used as active cleaning liquid an azeotropic preparation made of water and anone organic component is used in relative amounts of (100 x) percent by weightwt%: x percent by weightwt%, wherein x is in the range $0 < x \le 35$, preferably in the range $3 \le x \le 25$, and by special preference particularly preferably in the range $4 \le x \le 15$.
- 10. A process as described in method according to one of Claims 1 to 7, wherein there is used as active cleaning liquid an azeotropic preparation made of water and two organic components is used as the active cleaning liquid, preferably an azeotropic preparation made of water, dipropyleneglycolmono-n-propylether and an additional organic component.
- 11. A process as described in method according to one of Claims 1 to 10, wherein there is used as active cleaning liquid an azeotropic preparation made of water, a glycol ether, preferably dipropyleneglycolmono-n- propylether, and an additional organic component is used as the active cleaning liquid in relative amounts of 90 percent by weight wt%: (10 -y) percent by weight wt%: y percent by weight wt%, where in y is in the range $0 < y \le 5$, preferably in the range $0 < y \le 2$.